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UV-VIS Analysis on the Mechanism of the Sulfuric Acid-Catalyzed Dehydration of 2-Cyclohexen-1-OL

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UV-VIS ANALYSIS ON THE MECHANISM OF THE SULFURIC ACID-CATALYZED DEHYDRATION OF 2-CYCLOHEXEN-1-OL

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Abstract

This research initially set out to study the reaction kinetics of 2-cyclohexen-1-ol. This molecule, when undergoing an acid-catalyzed dehydration with 84.0% w/w sulfuric acid, was expected to follow the same pathway found in the later steps of the acid-catalyzed dehydration of cyclohexanol, namely, the formation of an allylic carbocation. Analysis using UV-Vis spectroscopy, however, showed that this was not the case. The primary absorption band in the UV-Vis spectrum of the dehydration of cyclohexanol, an allylic carbocation having λ_{max} at about 300 nm, was not visible in the UV-Vis spectrum of 2-cyclohexen-1-ol. Instead, a strong absorption band at 380 nm (indicative of a dienylic carbocation) was immediately formed, followed by its gradual decrease. Consequently, what was initially a study of the analogous relationship between the kinetics and mechanism of the acid-catalyzed dehydrations of cyclohexanol and 2-cyclohexen-1-ol turned into a focus studying the mechanism of the 2-cyclohexen-1-ol reaction. Further experiments were conducted in which the amounts of sulfuric acid and 2-cyclohexen-1-ol were varied. It was discovered that at low acidity, a prominent absorption band was observed at 260 nm, attributed to 1,3-cyclohexadiene. At high acidities, the prominent band was observed at 380 nm and corresponded to a dienylic carbocation. These experiments lead to the proposal that a concerted elimination step was responsible for the rapid formation of the dienylic carbocation.

Introduction

Cyclohexanol, when reacted with highly concentrated sulfuric acid, proceeds through the mechanism as illustrated in Figure 1. The hydroxy group is protonated by the acid and then leaves, forming a cyclohexanyl cation (I). Cyclohexene is then formed in an elimination step. Previously formed carbocation still present then abstracts a hydride from cyclohexene to form an

allylic carbocation (II). Prolonged duration of the reaction will lead to elimination of the adjacent hydride and formation of cyclohexadiene (III). Carbocation present in the reaction will again abstract an adjacent hydrogen, leading to a dienylic carbocation (IV). The reaction, if allowed to continue under appropriate conditions, has the potential to eventually form benzene.[1] The formation of the cycloalkenyl cations can be followed using UV-Vis spectroscopy, where the allylic carbocation (II) is visible in the region of 295-310 nm and the dienylic carbocation (IV) is visible in the 380 nm region. In addition, 1,3-cyclohexadiene (III) has an absorption maximum near 260 nm.

When reacted with highly concentrated sulfuric acid, 2-cyclohexen-1-ol was expected to form an allylic carbocation (II) directly after protonation of the hydroxyl group, and eliminating complexities of the earlier steps when beginning with cyclohexanol (Figure 2). After formation of the allylic carbocation (III), it was expected that the reaction would proceed similarly to the reaction of the cyclohexanol shown in Figure 1.

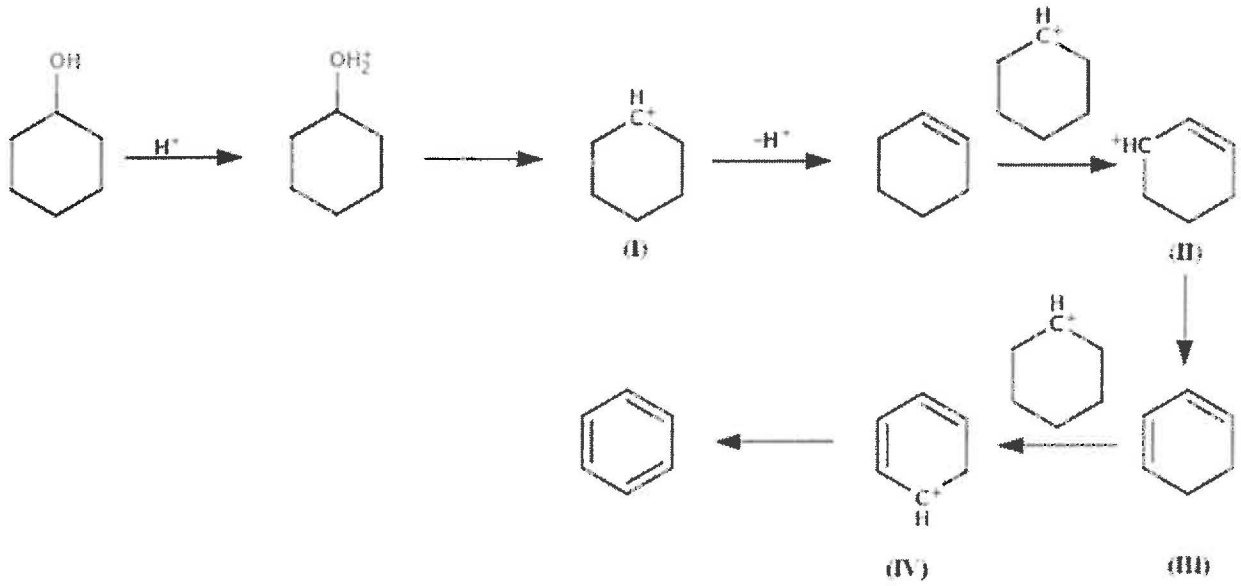

Figure 1. Mechanism of acid-catalyzed dehydration of cyclohexanol.

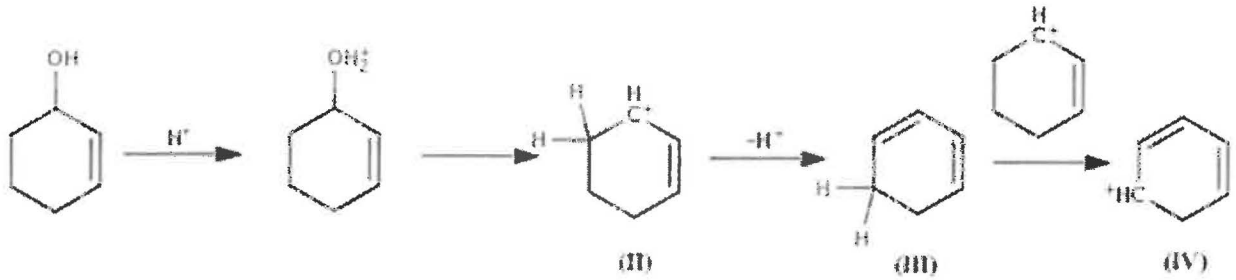

Figure 2. Proposed mechanism of acid-catalyzed dehydration of 2-cyclohexen-1-ol.

Initially, it was thought that the reaction of cyclohexanol and the similarities between the two mechanisms would help in the study of the mechanism for 2-cyclohexen-1-ol. Preliminary work, however, showed that the dehydration of 2-cyclohexen-1-ol underwent a different mechanism. As this became clear, the initial goal of analyzing kinetics data for the acid-catalyzed dehydration of 2-cyclohexen-1-ol narrowed in scope to focusing on analyzing the UV-Vis spectroscopy for mechanism determination.

Experimental Details

Spectra were obtained using a Shimadzu UV-2101PC UV-Vis scanning spectrophotometer connected to a constant temperature water bath (Neolab EX-111 Isotemp) circulating through a water-jacketed 100 mL beaker used to initiate the reaction by homogenizing the mixture. The experiment was carried out at at 49.1 °C. Spectra were obtained from 600 nm to 200 nm at a fast scanning speed 60 times over the course of 120 minutes (once every 2 minutes) or until the reaction reached equilibrium, whichever happened first. A solution of 84.0% w/w sulfuric acid (H_2SO_4) diluted from 96% w/w sulfuric acid (Sigma-Aldrich) was used as the reference solution. In the reaction initiation chamber, 10.0 mL of the sulfuric acid solution was introduced and allowed to reach thermal equilibrium. In a typical experiment, A 0.1 mL aliquot of 0.010 M 2-cyclohexen-1-ol (Aldrich) was introduced into the reaction chamber,

followed by brief homogenization with a magnetic stirrer and the transfer of the reaction solution into a screw-top quartz cuvette which was placed into the spectrophotometer. The time interval between the introduction of the 2-cyclohexen-1-ol into the reaction chamber and the appearance of the first band on the spectrophotometer was recorded using a stopwatch.

Results

Figure 3 shows the dependence of the absorption of the forming species against the wavelength at which it absorbed for the reaction of 0.1 mL of 0.010 M 2-cyclohexen-1-ol introduced into 10.0 mL 84% w/w sulfuric acid at 49.1 °C. Sixty readings were taken at equally spaced intervals over 120 minutes. The first reading was taken 44.0 seconds after initiation.

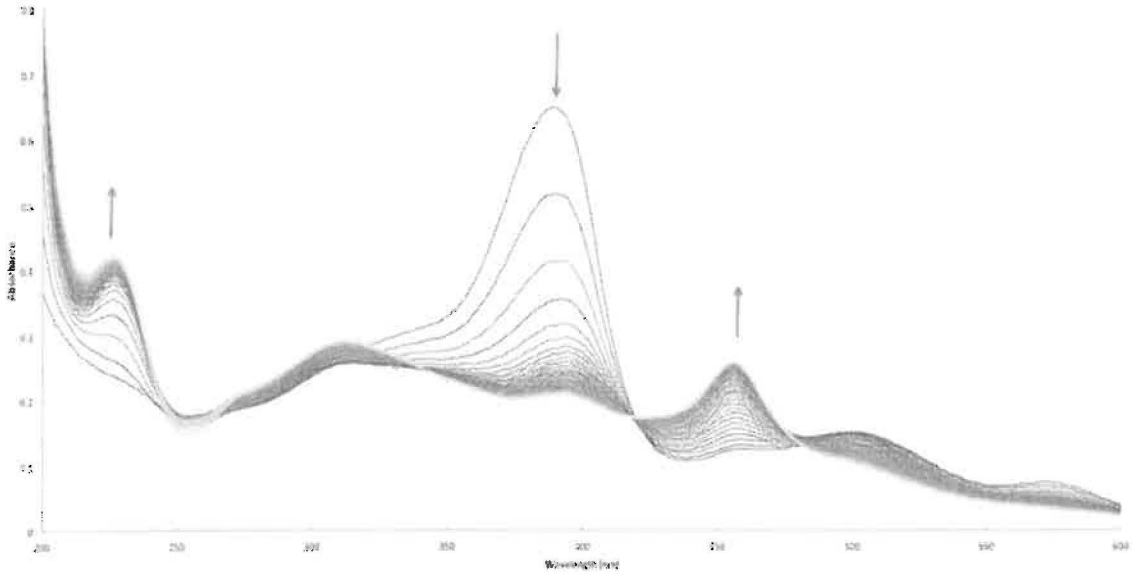

Figure 3. Absorption versus wavelength time series spectra of original experiment in which 0.1 mL of 0.010 M 2-cyclohexen-1-ol was introduced into 10.0 mL 84% w/w sulfuric acid at a temperature of 49.1 °C. Readings were taken 60 times over 120 minutes. The first spectrum began recording 44.0 seconds after initiation of the reaction.

Figure 3 shows a strong initial absorption near 380 nm, indicating the rapid formation of a dienylic carbocation,[1] followed by a gradual decrease. In addition, an isosbestic point occurring at about 420 nm indicates that the species on either side of that point have identical molar absorptivities at that particular wavelength, and that the increasing species is formed directly from the decreasing species.[2] The species increasing at 450 nm indicates a molecule of extended conjugation; its identity is unknown. In contrast, a band of absorption at 220 nm slowly increases over the trial period. The concentration of this unknown species increasing as the concentration of the dienylic carbocation decreased is not explained by the proposed mechanism in Figure 2. Noticeably absent was any absorption in the region of 290-310 nm, the region of absorption for an expected allylic carbocation.

The initial experiment was repeated and carried out at 31.2 °C in order to determine the effect of temperature changes on cycloalkenyl cation behavior. The results of this experiment are shown in Figure 4. The first reading was taken 48.4 seconds after initiation of the reaction.

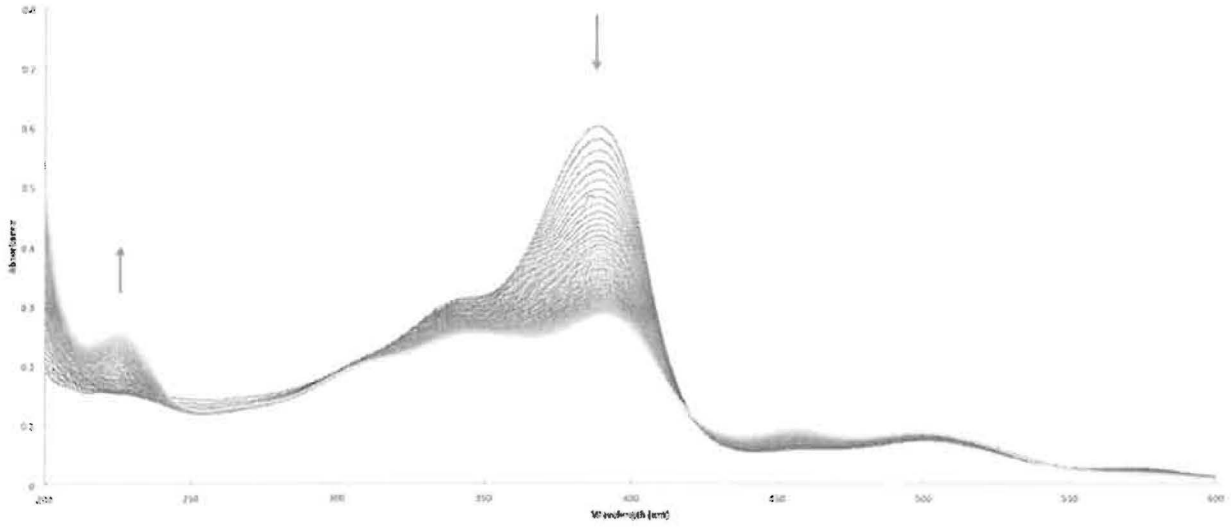

Figure 4. Absorption versus wavelength time series spectra of experiment in which 0.1 mL of 0.010 M 2-cyclohexen-1-ol was introduced into 10.0 mL 84% w/w sulfuric acid at a temperature of 31.2 °C. Readings were taken 60 times over 120 minutes. The first spectrum began recording 48.4 seconds after initiation of the reaction.

The results in Figure 4 showed that, while lowering the temperature did seem to slow the reaction down, the formation of the allylic carbocation was either still proceeding but at pace too fast to capture by lowering the temperature, or that the proposed mechanism was incorrect.

The primary experiment was repeated with 0.010 M cyclohexanol instead of 0.010 M 2-cyclohexen-1-ol, the results of which are shown in Figure 5. The first reading was taken 19.0 seconds after initiation of the reaction.

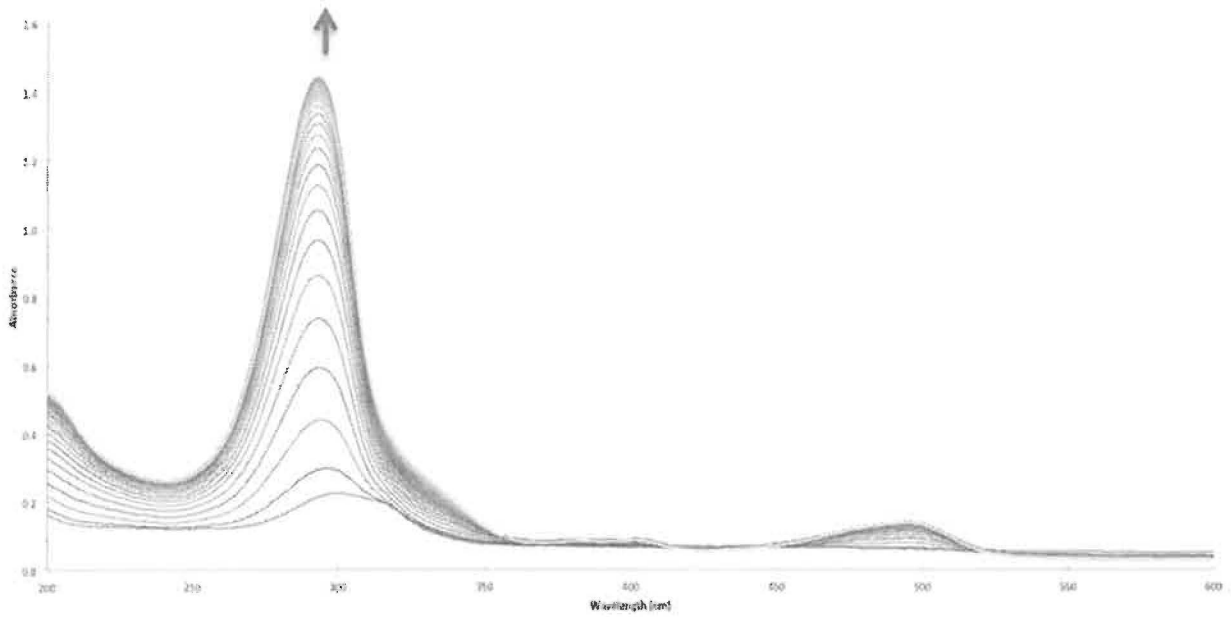

Figure 5. Absorption versus wavelength time series spectra of experiment in which 0.1 mL of 0.010 M cyclohexanol was introduced into 10.0 mL 84% w/w sulfuric acid at a temperature of 49.1 °C. Readings were taken 60 times over 120 minutes. The first spectrum began recording 19.0 seconds after initiation of the reaction.

The trial of cyclohexanol in Figure 5 followed the expected mechanism and the absorption spectra included the expected allylic carbocation absorption at 300 nm.[1] This indicates that there was likely little error in methodology of the experimental runs.

As acid concentration had a significant effect on the mechanism, an approach was taken to vary the acid concentration. First, the spectra of the unreacted 2-cyclohexen-1-ol solution using methanol as the reference were obtained. This was conducted at 33.2 °C with two readings taken 2 minutes apart. Figure 6 shows the spectra of this experiment. The purpose of this experiment was to determine a baseline for 2-cyclohexen-1-ol from which other spectra could be compared.

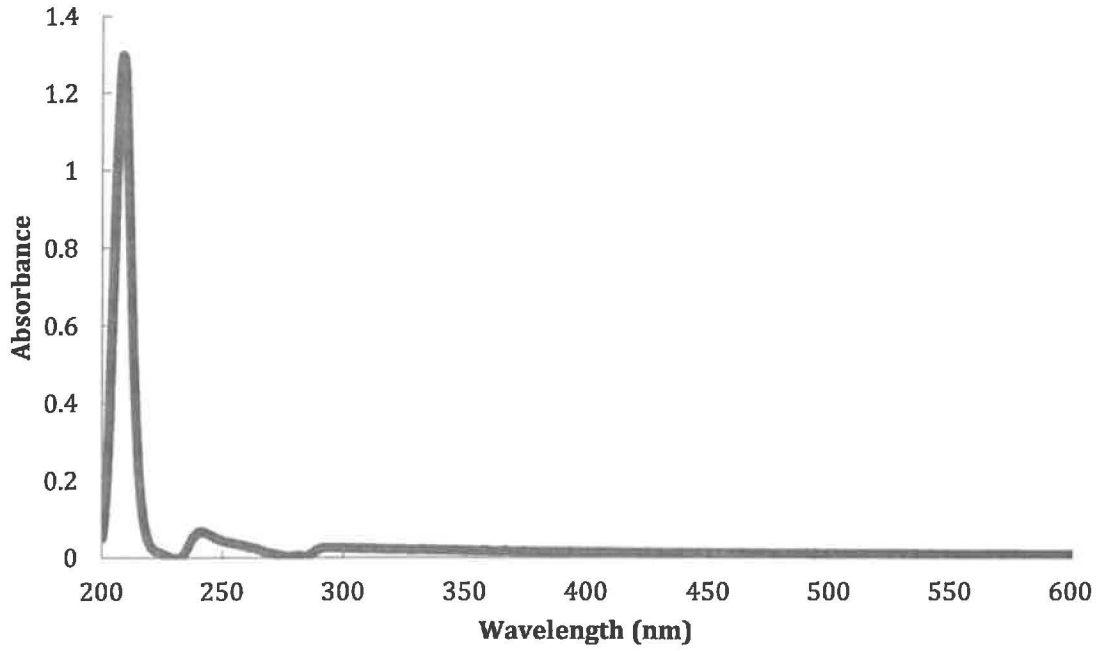

Figure 6. Absorption versus wavelength spectra of 0.010 M 2-cyclohexen-1-ol against methanol reference.

Figure 6 shows that 2-cyclohexen-1-ol did not show any significant absorption in the UV-Vis wavelength region of 210 nm to 600 nm. The strong absorption at about 210 nm is a result of using methanol as a reference, as methanol absorbs excessively at wavelengths below 210 nm.[3]

A drop of 84.0% w/w sulfuric acid was added to the cuvette that contained the 2-cyclohexen-1-ol, which was then run in the spectrophotometer, the results of which are shown in Figure 7. Ten readings, each taken two minutes apart, were obtained, and the reaction was carried out at 33.4 ^{O}C. The first reading was taken 9.6 seconds after initiation of the reaction.

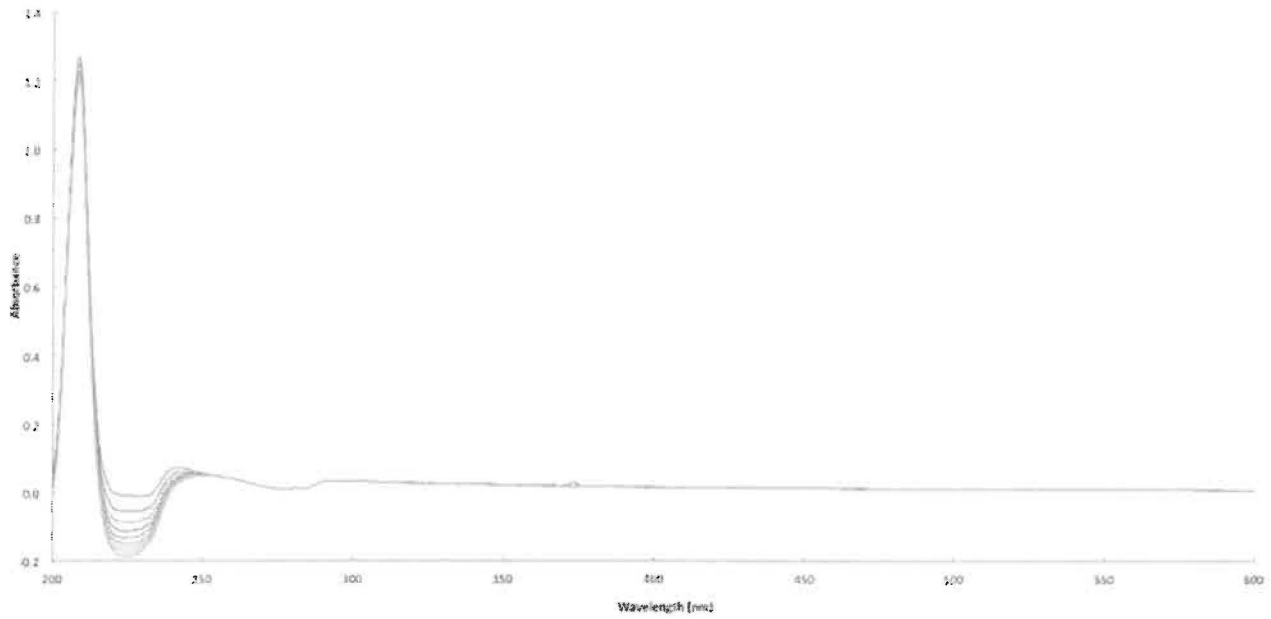

Figure 7. Absorption versus wavelength time series spectra of 0.010 M 2-cyclohexen-1-ol with one drop of 84.0% w/w sulfuric acid. The first spectrum began recording 9.6 seconds after initiation of the reaction.

The significantly lowered amount of sulfuric acid used in the experiment shown in Figure 7 was another attempt to study the earlier parts of the proposed mechanism in Figure 2 by slowing down the reaction. As the absorption spectra were not significantly altered from that of Figure 6 (aside from some anomalous negative readings), it was decided to increase the amount and concentration of sulfuric acid.

The quartz cuvette was refilled with 3.0 mL 0.010 M 2-cyclohexen-1-ol and five drops of 96% w/w sulfuric acid were added. Run against a methanol reference, twenty-three readings were taken, each two minutes apart, and the experiment conducted at 33.9 °C. The results are shown in Figure 8. The first reading was taken 18.4 seconds after initial reaction.

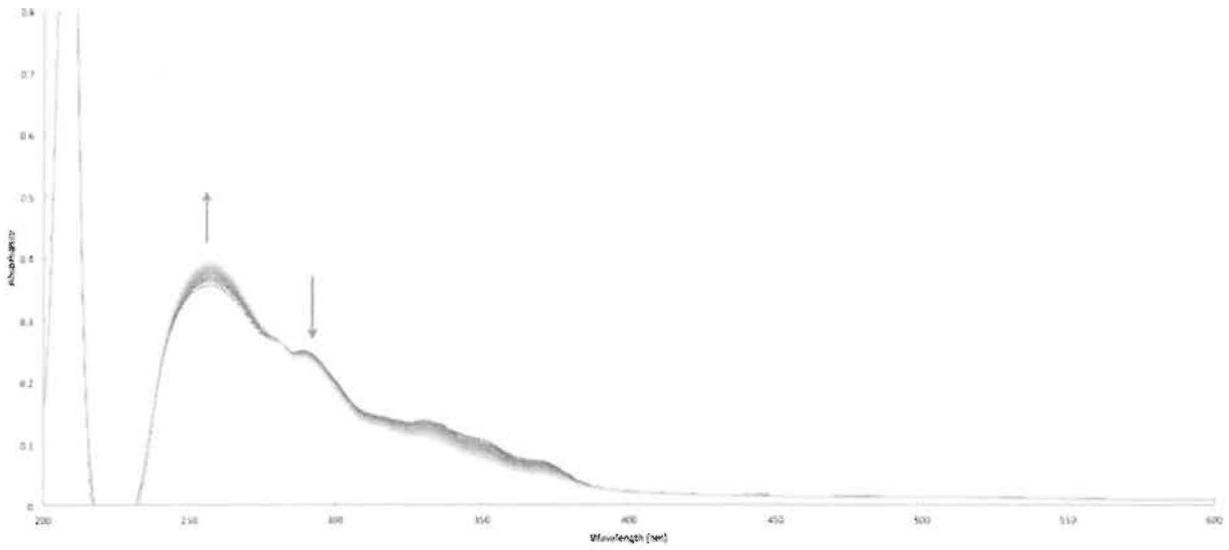

Figure 8. Absorption versus wavelength time series spectra of 0.010 M 2-cyclohexen-1-ol mixed with five drops of 96% w/w sulfuric acid. The first spectrum began recording 18.4 seconds after initiation of the reaction.

Figure 8 now shows a gradually increasing absorption around the 260 nm region, possibly indicating the presence of a diene (likely cyclohexadiene).[4] In addition, what appears to be a slight decrease in absorption appears around 295 nm, in the region of allylic carbocation absorption. Noticeably absent in Figure 8 is a strong λ_{max} at 380 nm, indicating that the experiment had reached equilibrium before arriving to the point of the dienylic carbocation's formation.

Considering that even this extreme modification of the initial experiment failed to produce an immediately defined allylic carbocation as proposed in Figure 2, an alternative mechanism was formulated. As Figure 8 shows the gradual initial increase of a cyclohexadiene, it was proposed that a concerted elimination reaction might be taking place. The proposed mechanism is shown in Figure 9.

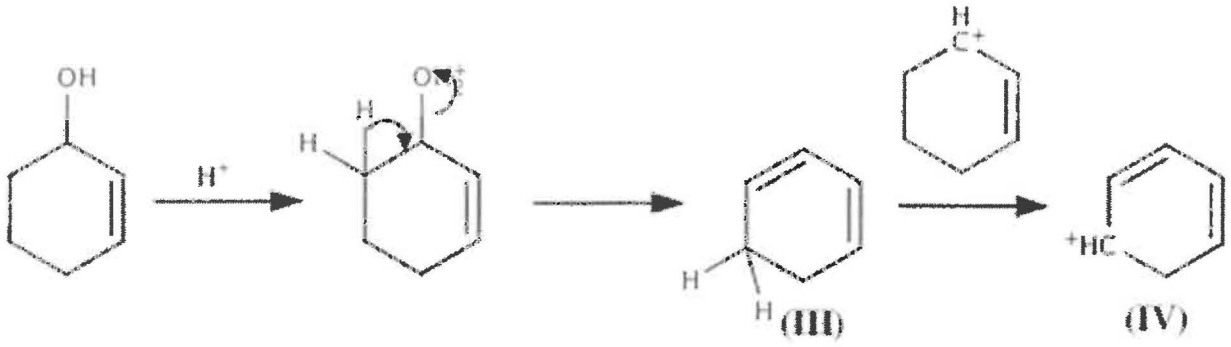

Figure 9. Proposed E1 mechanism for acid-catalyzed dehydration of 2-cyclohexen-1-ol.

In this proposed mechanism, the 1-hydroxy group on 2-cyclohexen-1-ol is protonated by sulfuric acid to form a protonated alcohol as in the original mechanism, a good leaving group. In concert, a hydrogen on the adjacent sp^3 carbon is eliminated, leading to formation of a double bond and the diene molecule (III) and continuing on to the formation of molecule (IV). The minor absorption near 300 nm in Figure 8, however, indicates the possible presence of the allylic carbocation, and that the originally proposed mechanism in which the hydroxyl group leaves to form a cyclohexanyl carbocation might still be at work parallel to the mechanism proposed in Figure 9. This still does not account for the rapidity of the initial formation of the band at 380 nm in the initial experiment (Figure 3). It was clear, however, that the particular mechanism at work in the acid-catalyzed dehydration of 2-cyclohexen-1-ol depends on the concentration of the acid.

Thus, the concentration of the sulfuric acid continued to be increased through several more experiments. Both the experimental and reference cuvettes were filled with 3.0 mL of 25.0% w/w sulfuric acid. To the experimental cuvette was also added 0.025 mL 0.010 M 2-cyclohexen-1-ol. Thirty-eight readings were taken, each two minutes apart, and the experiment

was conducted at 49.1 °C. The first reading was taken 17.2 seconds after initial reaction. The results are shown in Figure 10.

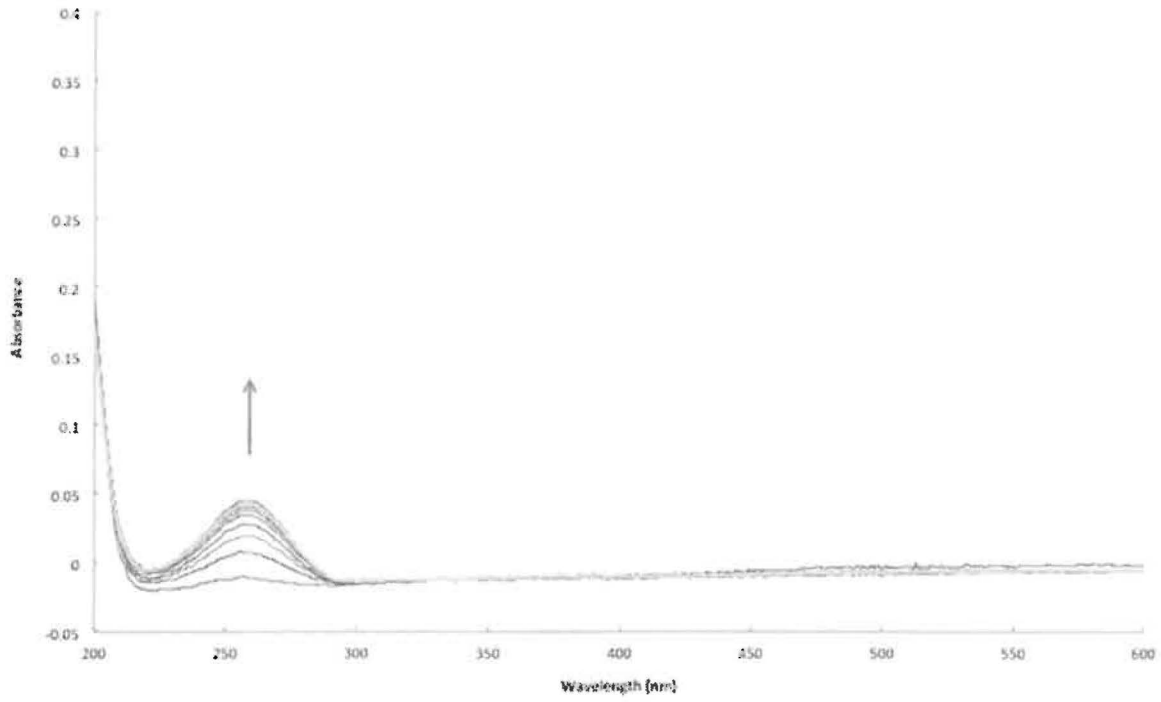

Figure 10. Absorption versus wavelength time series spectra of 3.0 mL 25.0% w/w sulfuric acid and 0.025 mL 0.010 M 2-cyclohexen-1-ol at 49.1 °C. The first spectrum began recording 17.2 seconds after initiation of the reaction.

The preceding experiment was repeated, replacing the 25.0% sulfuric acid in both the experimental and reference cuvettes with 42.0% sulfuric acid. The results are shown in Figure 11. The first reading was taken 12.1 seconds after initiation of the reaction.

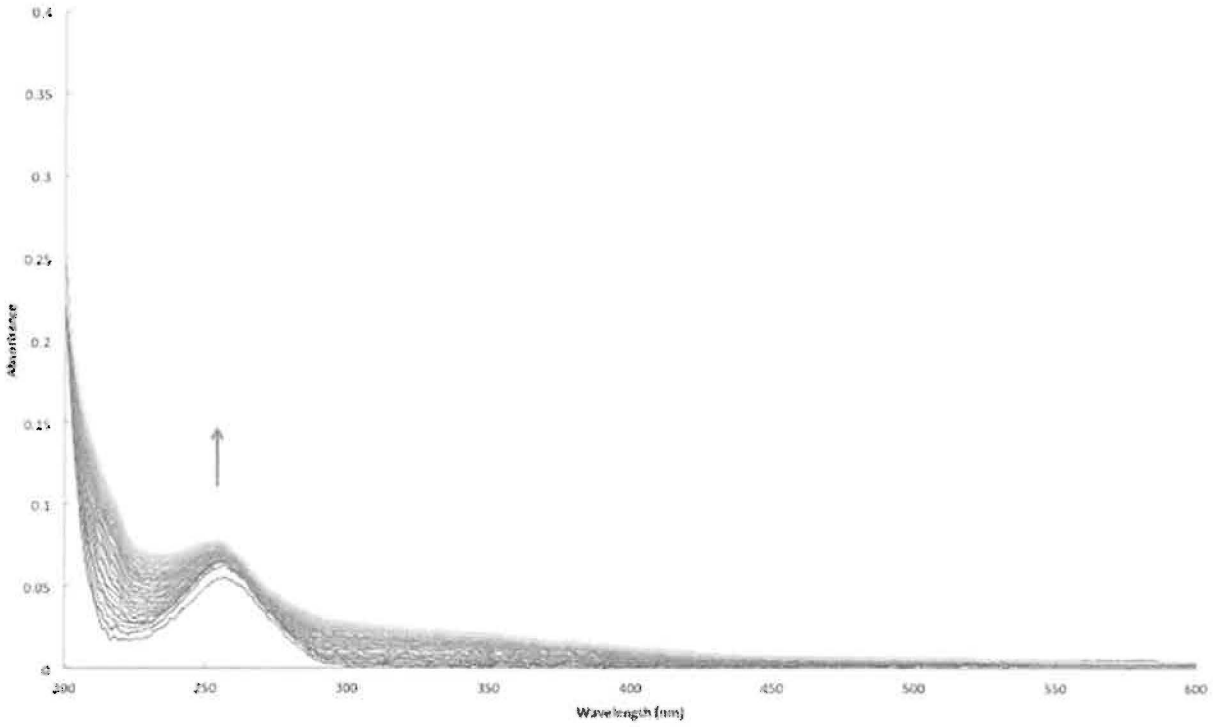

Figure 11. Absorption versus wavelength time series spectra of 3.0 mL 42.0% w/w sulfuric acid and 0.025 mL 0.010 M 2-cyclohexen-1-ol at 49.1 °C. The first spectrum began recording 12.1 seconds after initiation of the reaction.

The preceding experiment was repeated once more, replacing the 42.0% w/w sulfuric acid with 60.0% w/w sulfuric acid. Forty readings were taken instead of 38 readings, each two minutes apart. Spectral results are shown in Figure 12. The first reading was taken 16.1 seconds after initiation of the reaction.

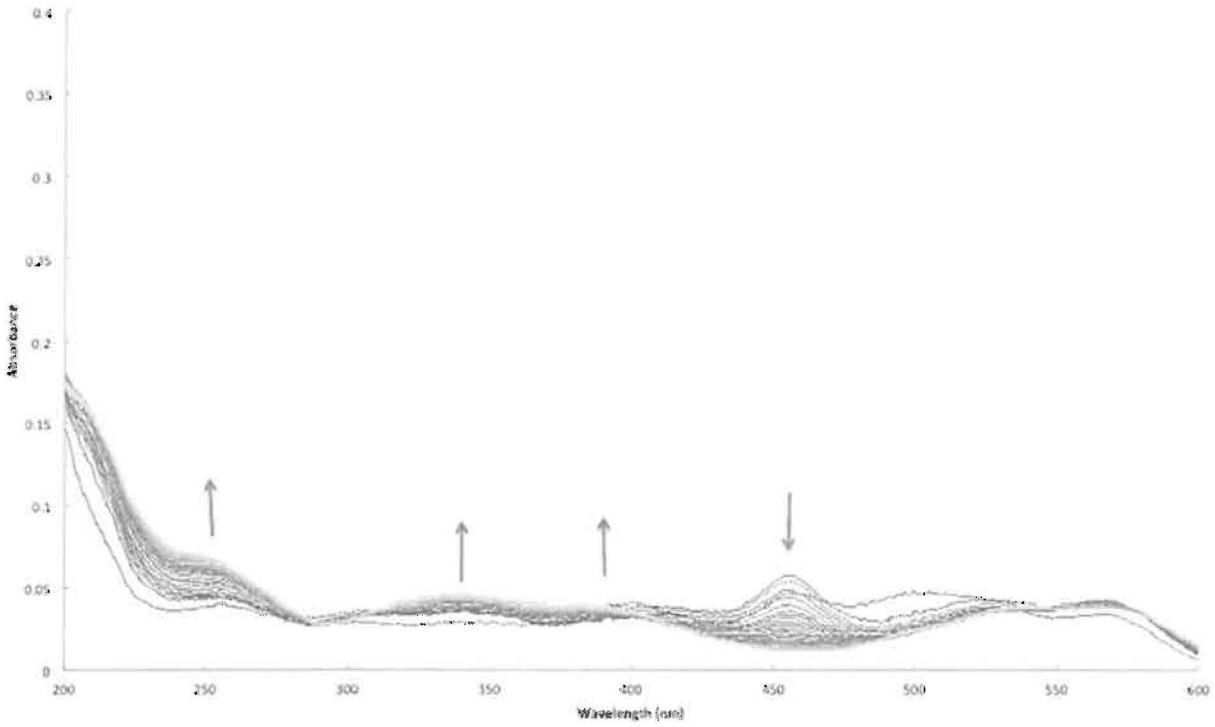

Figure 12. Absorption versus wavelength time series spectra of 3.0 mL 60.0% w/w sulfuric acid and 0.025 mL 0.010 M 2-cyclohexen-1-ol at 49.1 °C. The first spectrum began recording 16.1 seconds after initiation of the reaction.

The experiments carried out in Figures 10, 11, and 12 were conducted in order to determine in what concentration ranges of sulfuric acid solutions do certain species appear and disappear. Both Figures 10 and 11, the experiments conducted at 25.0% and 42.0% w/w sulfuric acid concentrations, respectively, show relatively strong, upward absorptions at 260 nm, indicating the formation of a diene, specifically 1,3-cyclohexadiene. There is, however, no significant presence of an allylic carbocation as would be indicated by absorption in the 290 nm region. There is also no significant absorption in the 380 nm region, signifying the lack of any dienylic carbocation. The spectra of the experiment carried out using 60.0% w/w sulfuric acid in Figure 12 begins to show some similarities to Figure 3, the initial experiment using 84.0% w/w

sulfuric acid. There is now evidence of diene at 260 nm and possible allylic carbocation formation at 310 nm. Of note is the increasing absorption at 380 nm, indicating possible dienylic carbocation formation, and the reappearance of the unknown species at 450 nm, demonstrating a decrease in absorption over time. In Figure 3, at 84.0% w/w sulfuric, these species show the reverse behavior, decreasing at 380 nm and increasing at 450 nm.

These later experiments made clear that acidity was a primary factor in determining whether this reaction followed a particular mechanism. They reaffirmed the conjecture deduced from Figure 8 that at lower acidities, a concerted elimination mechanism occurs. Cyclohexadiene has been found to be in a reversible equilibrium with 2-cyclohexen-1-ol when the former undergoes an acid-catalyzed hydration at lower concentrations of perchloric acid.[5] That the lower concentration experiments agree with this lends credence to the proposed mechanism in Figure 9.

Table 1 summarizes the various species found at each weight by water percentage of sulfuric acid. The experiments conducted at the higher acidities (60.0% and 84.0% w/w sulfuric acid) demonstrate a much more complex reaction mechanism. In Figure 12, the absorption of the cyclohexadiene at 260 nm increases at a faster rate than the absorption of the dienylic carbocation at 380 nm. This actually works well with the initially proposed mechanism in Figure 2 as all the species up until and including the dienylic carbocation (IV) are accounted for in Figure 12. When the acidity is raised to 84.0% and the dienylic carbocation starts off with a strong absorption and then gradually decreases, this could be evidence of a reversible equilibrium between the diene (III) and the cycloalkenyl cation (IV) in Figure 2 and that even higher amounts of acidity will shift that equilibrium toward formation of the diene.

Table 1. Summary of species observed at various sulfuric acid w/w percentages when reacted with 0.010 M 2-cyclohexen-1-ol.

Sulfuric Acid w/w % in 0.010 M 2-Cyclohexen-1-ol	**λ_{max} observed (nm)**
84.0% (1 drop)	none
96.0% (5 drops)	256 (increasing), 290 (decreasing)
25.0%	256 (increasing)
42.0%	256 (increasing)
60.0%	252 (increasing), 290 (increasing), 380 (increasing), 452 (decreasing)
84.0%	238 (increasing), 383 (decreasing), 452 (increasing)

Conclusion

As the proposed mechanism for the acid-catalyzed dehydration of 2-cyclohexen-1-ol was initially hoped to be an analogous reaction to the dehydration of cyclohexanol, initial expectations were for this research to be rather straightforward in scope. However, as the first UV-Vis spectra were taken, it became clear that this was not the case. While lowering the temperature did not clarify mechanistic information, the experiment conducted in Figure 8 was considered the breakthrough experiment in elucidating that acidity modification was the direction in which to take this research, ultimately leading to the conclusion that the reaction follows different mechanisms depending on the acid concentration.

The primary objective of any further research would be the final determination of the mechanism for the acid-catalyzed dehydration of 2-cyclohexen-1-ol. Further research that could be conducted would involve varying of the acid concentration in the experiment in order to determine whether the changes noted between the experiments occur gradually or all at once at certain sulfuric acid concentrations. The area of most interest in particular would be the range between 42.0% and 60.0% (Figures 10 and 11). In addition, analysis on this reaction's kinetics at

each acid concentration would prove useful for the determination of rate constants and orders at various stages throughout the reaction.

References

1. Fini, A.; Fazio, G.; Tonelli, D.; Roda, A.; Zuman, P. *Il Farmaco*. **1992,** 47, 741-752.
2. McNaught, A.D.; Wilkinson, A. *IUPAC Compendium of Terminal Technology*. 2nd ed. Blackwell Scientific Publications: Oxford. **1997**; 1129.
3. Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics.* 84th ed. CRC Press: Boca Raton, Fla. **2003-2004**; 8-129
4. Zuman, P. *Microchemical Journal*. **1993**, 43, 10-34.
5. Jensen, J.L.; Carré, D.J. *J. Org. Chem.* **1971,** 36, 3180-3183.